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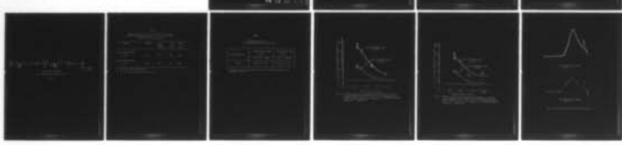

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SURFACE CHEMICAL COMPOSITION-DEPTH PROFILE OF POLYETHER POLYURETHANEUREAS AS STUDIED BY FT-IR AND ESCA.

by

(10) C.B. Hu [redacted] C.S. Paik Sung

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Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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C.B. Hu and C.S. Paik Sung
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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ABSTRACT

Chemical composition-depth profile in the range covering 100^{o}A to 2μ was obtained with well-characterized polyether poly(urethaneurea) elastomers by combining FT-IR internal reflection technique with ESCA. In FT-IR technique, either the incident angle of the internal reflection attachment was changed or a thin film, which is transparent to most of IR radiation, was cast directly on the reflection plate to reduce the depth of the IR beam penetration in order to obtain surface chemical composition at various depths. Our results show that the flexible, soft segment is more abundant on the surfaces, especially at the air facing surface, as compared with the bulk composition. This trend is observed not only in the first 100^{o}A, but also into a much deeper depth, such as 1μ. Our results suggest that the migration of oligomers (∿ 5000 MW) such as trimers or pentamers, which have soft segments at both ends is responsible for the observed high content of soft segment on the surface. The presence of the oligomers are indicated by GPC and the extraction studies support that they have higher content of soft segment when compared with the bulk composition.

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INTRODUCTION

Polyether polyurethanes or polyurethaneureas are multi-segmented copolymers consisting of short, hard segments (urethane or ureas) connected with soft, rubbery polyether segments. The properties of these polymers, as thermoplastic elastomers, are primarily attributable to the phase segregation of soft and hard segments, leading to the formation of hard segment domains, which are dispersed in the rubbery polyether matrix. A variety of compositional and processing variables are known to affect the degree of bulk phase segregation and the volume fractions of the hard segment domains in bulk[1,2]. Furthermore, at or near the surface, the thermodynamic and kinetic factors may alter the ratio of volume fractions of hard to soft segment phases. Our previous work with two commercially available polyurethane materials, Avcothane™ and Biomer™, indicated that the concentration of the soft segment incresed sharply near the surface, especially at the surface which faced air during the solvent casting procedure[3,4,5]. Due to the proprietary nature of these two commercial polymers, it was difficult to establish bulk structure-surface property relationships. However, in other block copolymer systems, similar types of behavior have been observed. For example, Thomas and O'Malley reported that in polystyrene-polyethylene oxide block copolymers, the amorphous polystyrene was more abundant near the surface, as observed by ESCA[6]. Also McGrath et al reported that in polycarbonate-polydimethylsiloxane block copolymer, ESCA scans mainly showed the polydimethylsiloxane spectra[7]. These results obtained by ESCA provide information on the surface chemical composition only in

the first 100Å layer. It will be very useful to have the surface chemical composition-depth profile not only for the first 100Å, but also covering a couple of micron. Toward this goal, we have combined FT-IR multiple internal reflection technique and ESCA analyses and obtained surface chemical composition-depth profiles with well-characterized[8,9] amorphous polyether poly(urethaneureas), which is a well phase-segregated system in the bulk. In FT-IR internal reflection technique, either the incident angle of internal reflection attachment was changed or a thin film (which is transparent to most of IR radiation) was cast on the reflection plate to reduce the depth of the IR beam penetration, thus enabling us to do depth profiling.

EXPERIMENTAL

Materials. Two samples of polyether polyurethaneureas based on 2,4 toluene diisocyanate (2,4 TDI), ethylene diamine (ED), and polytetramethylene oxide (PTMO, M.W. 1000 or 2000) were used. The chemical structure is shown in Scheme I. The synthesis of these polymers by solution polymerization has been described before[8]. One sample has the molar ratio of 2:1:1 for 2,4 TDI:ED:PTMO (M.W. 1000), while the other sample has the molar ratio of 4:3:1 for 2,4 TDI:ED:PTMO (M.W. 2000). The average urea content (hard segment content) in the bulk is the same as 30% for both samples. The molecular weight by GPC and the thermal transitions for these two polymers are summarized in Table 1. Both samples show extensive phase segregation with the latter being even better in phase segregation than the former. Both

samples are completely amorphous. Polymer films were cast from 5% DMF solution and dried under vacuum oven at 50°C for at least 2 days.

Methods. FT-IR internal reflection spectra were obtained by using a KRS-5 reflection plate at the incident angle of either 45° or 60° with Wilks Model #9 internal reflection attachment. Calculations on the equation that Harrick derived[10] show that the surface depth that the IR beam penetrated was about 1.9μ and 1.3μ for 45° and 60° incident angle, respectively. Kel-F82 copolymer from 3M Company was used to reduce the penetration of the IR beam by casting directly on the KRS-5 plate[3]. The thickness of this film was 0.66μ, therefore, at the incident angle of 60°, the effective depth that was averaged was 0.6μ. The spectra of Kel-F82 was subtracted from the internal reflection spectra by digital subtraction. ESCA scans were obtained on a Physical Electronics Industries, PHI model 548 ESCA/Auger Electron Spectrometer by using MgK_{α} radiation at 10^{-8} torr vacuum at ambient temperature. The window was set at 10 ev and the scan rate was 0.01 ev/sec with pass energy of 15 ev. The sensitivity of each element was adjusted to be the same so as to compare the area directly.

Results and Discussion

Before we present the results on surface chemical composition, it will be useful to comment briefly on the bulk phase segregation and the domain organization of the two samples we chose for the study. Both of these samples are polyether poly(urethaneureas), which have 2,4 toluene diisocyanate and ethylene diamine as hard segment and poly(tetramethylene oxide) as soft segment, as shown in Scheme I.

One sample (2:1:1 composition of 2,4 TDI:ED:PTMO 1000) has 1000 M.W. polyether while the other (4:3:1 composition of 2,4 TDI:ED:PTMO 2000) has 2000 M.W. polyether as the soft segment. However, the total weight percentage of the hard segment (urea) and the soft segment has been controlled to be the same. In both of these samples, the phase segregation and domain structure were greatly improved as compared with diol extended analogs, as evidenced by the lower Tg of the soft segment phase and the higher Tg of the amorphous hard segment domain[11] (refer to Table I). The presence of the amorphous, relatively pure hard segment domain was supported by small angle x-ray scattering and DSC studies for both samples[12]. Between these two, PTMO 2000 polymer exhibited better phase segregation than for the PTMO 1000 polymer in terms of purity of soft segment phase. In PTMO 2000 sample, the soft segment phase is almost pure, free from solubilized hard segment while in the PTMO 1000 sample, the soft segment phase contains an appreciable amount of solubilized hard segment[13].

With this background information stated, we will now discuss the results on the surface chemical composition obtained with these two samples. Figure 1 shows the plot of the relative ratio of soft segment/hard segment as a function of the averaged surface depth for the air facing surface of both samples. The ether absorption peak at 1110 cm^{-1} was used as representing soft segment content whereas both of the urea carbonyl peak at 1640 cm^{-1} and aromatic peak at 1600 cm^{-1} were used as representing the hard segment to confirm the reliability of the data. There seems to be a good agreement as shown in Figure 1

between the two values; i.e. $A_{1110\ cm^{-1}} / A_{1640\ cm^{-1}}$ (triangles) and $A_{1110\ cm^{-1}} / A_{1600\ cm^{-1}}$ (squares) as the ratio of soft segment/hard segment. These intensity ratios were obtained after calibrating for the differences in the penetration depth of the IR beam since the penetration depth at 1110 cm^{-1} would be somewhat greater than that at 1600 cm^{-1} or 1640 cm^{-1}. It is also useful to point out that the data plotted in Figure 1 reflects the composition averaging the specified depth from the surface, rather than the composition at that depth. Also the specified depth is the theoretical maximum value when assuming ideal contact between sample and crystal plate. Some interesting features can be pointed out from Figure 1. For both samples, the relative ratio of soft segment/hard segment increases when one comes near the surface. When the averaged depth is 1.9μ, this ratio for PTMO 1000 sample is about the same as the bulk composition (as obtained by the transmission IR technique) but the ratio for PTMO 2000 sample is slightly higher than the bulk composition. But nearer the surface, as indicated by two other experimental points, the data for the PTMO 2000 sample shows greater extent of non-uniformity of the components than for PTMO 1000 sample in such a way that more soft segment is found than the hard segment. Figure 2 shows an analogous plot for the glass facing surface of both samples. Very similar trend is observed between Figure 1 and Figure 2, except that for PTMO 2000 sample, a slightly higher ratio of soft segment/hard segment was observed in air facing side than for the glass facing side. Since it is difficult to achieve the contact efficiency of 100% between

sample and the crystal plate, there is a certain amount of uncertainty in the depth values in Figure 1 and Figure 2. However, it is reasonable to expect the similar contact efficiency throughout our experimental procedure. Therefore, the trend would remain the same, even though the curves would be shifted toward the shorter depth.

For the surface chemical composition in the first 100 Å or so, ESCA analysis was used. Since nitrogen is originated only from hard segment and the oxygen is mostly from soft segment, the ratio of O/N ESCA peaks is used as representing the relative content of soft segment/ hard segment. The ratio of O/N in the bulk can not be directly measured by ESCA but has been estimated from the composition to be about 4. The ESCA results on the surface composition of these polyurethanes are summarized in Table 2. It is obvious from Table 2 that the ratio of O/N on surfaces of both samples is greater than that for the bulk; i.e., more soft segment is found on the surfaces than would be expected from the bulk average. When two samples are compared with each other, PTMO 2000 sample exhibits this trend to a much greater extent than PTMO 1000 sample. With the same sample, air surface shows higher ratio of O/N. These ESCA results appear to be consistent with the trend indicated by FT-IR results.

Other researchers found similar behavior of non-uniform distribution in other block copolymers by ESCA and have interpreted it due to the lower surface energy characteristic of the component more abundant on the surface[7]. Certainly, in our systems, soft segment polyether has lower surface energy than the hard segment (aromatic urea). However,

our results show that the non-uniform distribution is observed at a depth much beyond what would be expected since the length of the soft segment can not be more than a couple of hundred angstroms. A careful examination of GPC scans of our polymers show a small amount of lower molecular weight ($\sim$ 5000 M.W.) species as indicated in Figure 3. The relative amount of these species is about the same for both samples. In order to separate these lower molecular weight species, the polymer (4:3:1 composition of PTMO 2000 series) was stirred in DMF at room temperature for a very brief time (15 minutes). Usually a couple of hours of stirring is required for a complete solution of these polymers. Therefore, the extractables obtained after such a brief time of stirring are expected to be composed of mainly lower molecular weight species. IR transmission spectra of the extractables taken after the solvent is dried shows the intensity ratio of $A_{1110cm^{-1}}/A_{1650cm^{-1}}$ to be about 4, which indicates that the lower molecular weight species have much higher soft segment concentration than the bulk composition. Therefore, these species are likely to be trimers or pentamers such as Soft-Hard-Soft, Soft-Hard-Soft-Hard-Soft with soft segments at both ends. During the drying process these trimers and pentamers would migrate toward surfaces. The migration would be expedited since the solvent, dimethylformamide appears to be a better solvent for PTMO (soft segment) than for the hard segment. Since these oligomers would contain much higher content of soft segment than the bulk average, the surface chemical composition would be richer in the soft segment. This trend is what we observe by FT-IR and ESCA techniques. The fact that the PTMO 2000 sample exhibits a greater extent of this trend by about a twofold as compared with

the PTMO 1000 sample can be explained since the oligomers of PTMO 2000 would have about twice the ratio of soft segment/hard segment as compared with those of PTMO 1000, as long as the oligomers have PTMO ends.

Conclusion

The surface chemical composition depth profile of well-characterized, well phase-segregated polyether polyurethaneureas were determined by a combination of FT-IR and ESCA techniques, in the surface depth range of 100A° to 2μ. Our results show that the flexible, soft segment is more abundant on the surfaces, especially at the air surface as compared with the bulk composition. This trend is observed not only in the first 100A° but also when a much deeper depth such as 1μ level is averaged. Our results suggest that the migration of oligomers (∿ 5000 MW) such as trimers or pentamers, which have soft segments at both ends is responsible for the observed high content of soft segment on the surface. The presence of the oligomers are indicated by GPC and the extraction studies support that they have higher content of soft segment when compared with the bulk composition.

Acknowledgement

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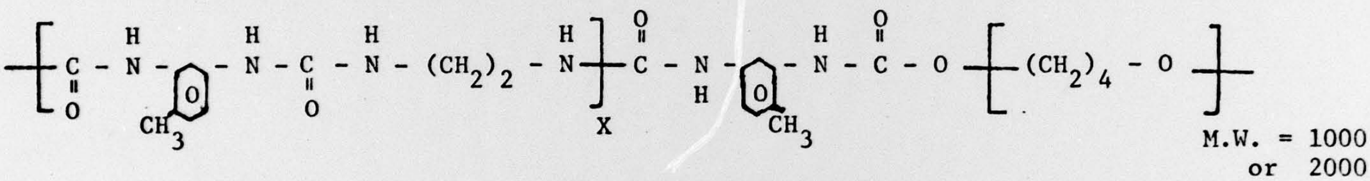


2,4 TDI-ED-PTMO 1000

or 2,4 TDI-ED-PTMO 2000 Polymers

SCHEME I

TABLE I

Characterization of Polyether Polyurethaneureas based on 2,4 Toluene Diisocyanate, ethylene diamine and polytetramethylene oxide.

Sample	$Mn x 10^{-3}$	Urea wt.% (bulk)	Tg_1* (°C)	Tg_2** (°C)
2,4 TDI-ED-PTMO 1000 2:1:1	21	30	-53	192
2,4 TDI-ED-PTMO 2000 4:3:1	36	30	-74	190

* Tg of the soft segment phase

** Tg of the amorphous hard segment domain

TABLE 2

ESCA Intensity Ratios
of two Polyether Poly (urethaneureas)

Intensity Ratio	2,4TDI-ED-PTMO 1000 2:1:1		2,4TDI-ED-PTMO 2000 4:3:1	
	Air	Glass	Air	Glass
O/N*	12.21	6.01	19.36	12.53

* represents the relative ratio of soft segment/hard segment on the surface (~100 A°).

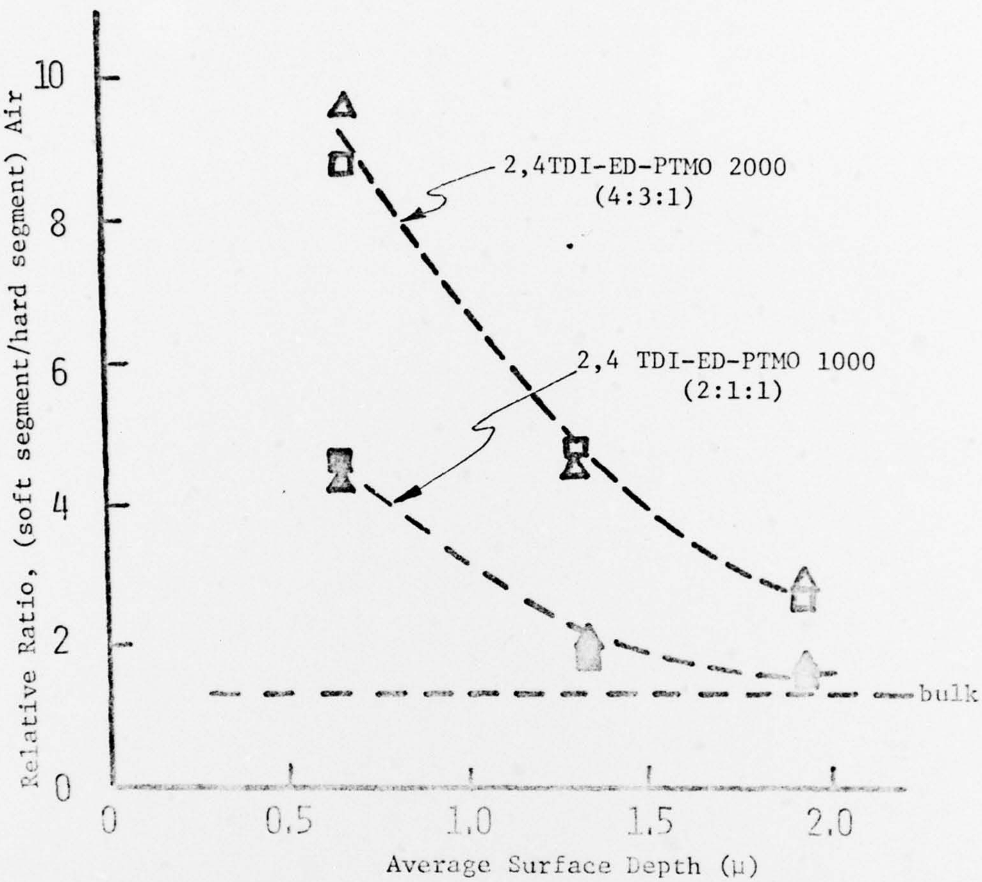


Fig. 1. Relative ratio of soft segment/hard segment as a function of the averaged surface depth for the air facing surface. (Square points: $A_{1110\ cm^{-1}}$ / $A_{1600\ cm^{-1}}$; triangular points: $A_{1110\ cm^{-1}}$ / $A_{1640\ cm^{-1}}$)

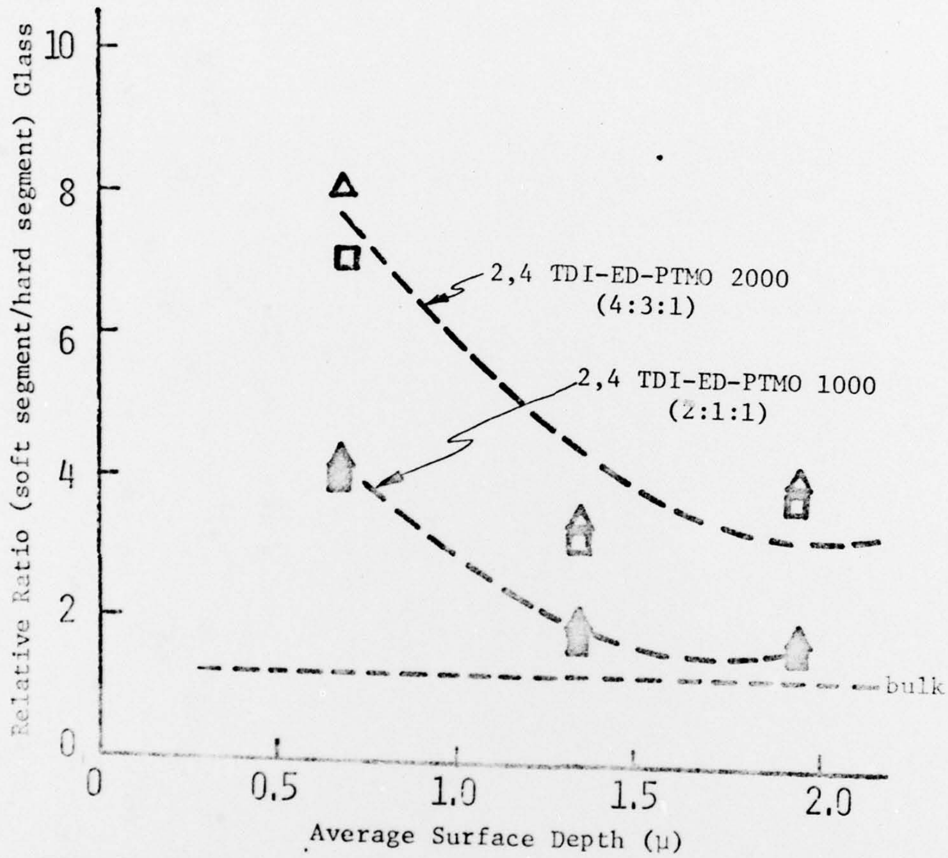
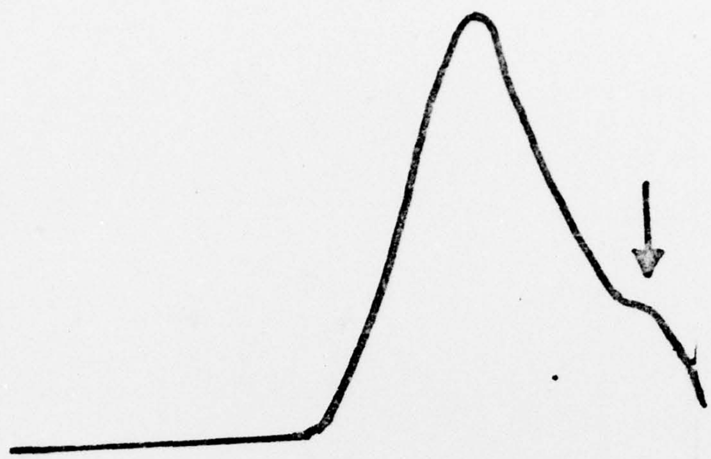
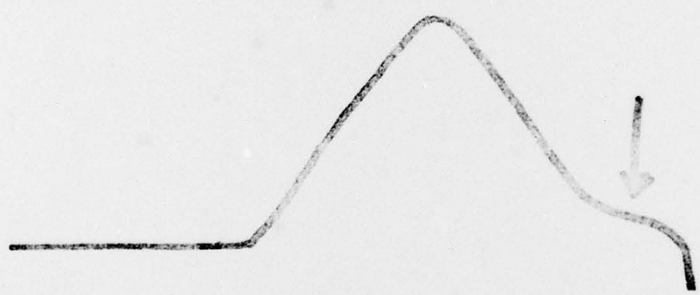


Fig. 2. Relative ratio of soft segment/hard segment as a function of the averaged surface depth for the glass facing surface. (Square points: $A_{1110\ cm^{-1}}$ / $A_{1600\ cm^{-1}}$; triangular points: $A_{1110\ cm^{-1}}$ / $A_{1640\ cm^{-1}}$)



2,4 TDI-ED-PTMO (1000)
2:1:1



2,4 TDI-ED-PTMO (2000)
4:3:1

Fig. 3. GPC Scans for polyether polyurethaneureas